Photosensitivity in Ge-doped silica optical waveguides and fibers with 193-nm light from an ArF excimer laser

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Photosensitivity in optical fibers and waveguides has been associated with the bleaching of an absorption band located near 5.0 eV (or 242 nm). We present new results for Bragg grating formation and UV bleaching experiments carried out using 193-nm light from an ArF excimer laser instead of the usual laser sources operating near 242 or 248 nm.

Since the discovery of photosensitivity in germanosilicate optical fibers using 488-nm light from an Ar-ion laser,[1] this phenomenon has been associated with the presence in GeO_2 of an absorption band located near 5.0 eV, or 242 nm (absorbing at 488 nm through a two-photon process).[2] Accordingly, the efficiency of the process increases greatly by use of strong in-band UV laser light instead of reliance on two-photon absorption at blue wavelengths.[3] The absorption band appears to be due to oxygen-deficient defects of the GeO_2–SiO_2 matrix,[4–5] and its amplitude varies widely among different types of fiber and planar waveguides. Apart from increasing the Ge doping, which is not always practical, various techniques have been demonstrated recently to enhance the photosensitivity of silica-based optical waveguides.[6,7] In particular, standard telecommunication optical fibers and planar silica-on-silicon waveguides do not show much natural photosensitivity. Throughout these developments, the bleaching of the 5.0-eV band has always been held responsible for triggering the complex electron transfer phenomena that result in permanent refractive-index changes at visible and infrared wavelengths. This was confirmed in the experiments of Atkins and Mizrahi,[8] in which direct measurements of the bleaching of the band were carried out on thin fiber sections.

Our decision to use a shorter wavelength for photosensitivity experiments was triggered by the observation[9] (confirmed in our laboratory) that no absorption near 5.0 eV appears in some H_2-loaded Ge-doped silica samples in spite of the fact that their photosensitivity increased greatly as a result of the loading. Furthermore, the dominant spectroscopic absorption changes associated with the photosensitive refractive-index changes seem to be occurring at wavelengths shorter than 200 nm[8,9]

In this Letter the results of two related experiments are presented: first, we measured the absorption changes induced by an excimer laser in planar samples of Ge-doped silica, using both 248-nm light (from a KrF excimer laser) and 193-nm light (from an ArF excimer laser). Second, we fabricated Bragg gratings in weakly photosensitive fiber at both wavelengths (248 and 193 nm) and examined their thermal stability.

For the measurement of photoinduced absorption changes we used 5-μm-thick planar optical waveguides made of Ge-doped silica on 1-mm-thick synthetic silica substrates. The doped layers were deposited by the flame hydrolysis technique[10] and contained 7 mol. % of GeO_2. As fabricated, the samples are transparent in the 190–400-nm wavelength region and insensitive to UV laser light. The photosensitivity is induced by H_2 loading at room temperature and pressures from 7000 to 12,000 kPa.[7] From diffusion calculations over the 5-μm-thick doped layer[11] we find that the concentration of dissolved molecular H_2 saturates in the whole layer after approximately 5 h. For longer periods in the pressure chamber (up to several weeks), the H_2 begins to react with weak bonds in the glass matrix, and strong absorption bands develop near 242 nm and also at shorter wavelengths. One can speed up this long-term reaction by heating the H_2-loaded glass.[9] The absorption measurements were carried out perpendicularly to the surface of the layer in a double-beam Cary 3 UV–visible spectrophotometer from 190 to 400 nm. Bleaching was induced with a Lumonics excimer laser operated at 50 pulses/s with pulse energy densities of 120 mJ/cm^2 at 248 nm and 40 mJ/cm^2 at 193 nm.

The fabrication of Bragg gratings was performed in a bend-insensitive germanosilicate fiber from Alcatel containing approximately 7 mol. % of GeO_2 in the core, similar to the fiber used in Ref. 8 and to our planar samples. We purposely chose to use a weakly photosensitive fiber (and not to load it with H_2) to be able better to quantify the difference in response for the two wavelengths of excitation. The Bragg gratings were written by the phase mask technique[12] and have a 0.53-μm period. The amplitude of the in-

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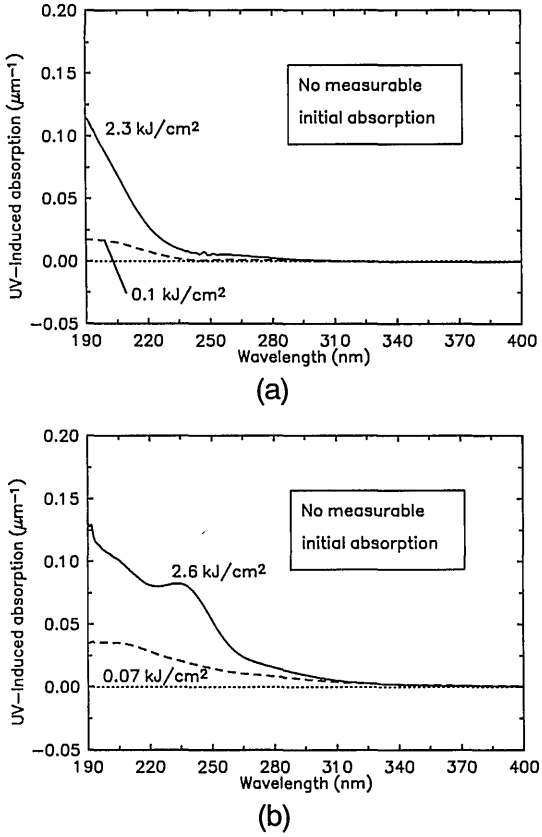

Fig. 1. Spectra of absorption changes induced by UV light in initially transparent H_2-loaded Ge-doped silica: (a) at 248 nm, (b) at 193 nm. The two curves in each graph correspond to different cumulative UV doses.

duced refractive-index modulation was inferred from the reflectivity of the gratings.

Typical results for the Ge-doped layers loaded with H_2 for short time periods (less than seven days) are shown in Fig. 1. In this case, no initial absorption that is due to the dissolved molecular H_2 can be detected. Therefore the absorption at UV wavelengths is due mainly to the tail of the ~160-nm vacuum-UV band gap of silica: this absorption is slightly higher at 193 nm than at 248 nm but smaller than 0.5 cm^{-1} in either case. In spite of this, we see that strong absorption changes occur in the doped layer on exposure to UV light. At 248 nm [Fig. 1(a)] the absorption increase appears to be centered at a wavelength shorter than 190 nm and shows no distinct feature at longer wavelengths. In particular, there is no sign of an absorption band near 242 nm. On the other hand, with 193-nm exposure [Fig. 1(b)] a distinct absorption peak is generated near 242 nm, with a weak feature near 210 nm in addition to the tail of a strong absorption below 190 nm. The formation of the 242-nm band seems to occur in the later stages of exposure (higher dose), since it does not appear in the low-dose result.

Figure 2 shows the results obtained with samples pressure loaded with H_2 for longer periods, resulting in the formation of absorption bands near 242 nm and at wavelengths shorter than 190 nm, as seen in the insets. The sample used for Fig. 2(a) spent six weeks in H_2, whereas that of Fig. 2(b) spent almost ten weeks in the pressure chamber. The initial absorption spectra in these cases are similar to those observed by Atkins and Mizrahi[2] in standard optical fiber. The changes observed after 248-nm exposure [Fig. 2(a)] also follow the trend observed in optical fibers. The 242-nm band is bleached quickly and completely after a relatively small UV dose, but the absorption continues to increase significantly at shorter wavelengths with further exposure to the bleaching radiation. As shown in Fig. 2(b), exposure to 193-nm light results in a quite different spectrum of absorption changes: two bands appear early in the exposure, centered near 220 and 260 nm, which seem to merge into a strong 225-nm peak at higher UV dose. Little bleaching of the high initial absorption at 193 nm can be seen. A feature of interest of these results is that the strongest absorption increases have been achieved in the case shown in Fig. 2(a), i.e., bleaching at 248 nm when there is an initial strong 242-nm band (note the different vertical scale). We also point out that, while the absorption changes shown have been obtained with comparable UV doses (near 0.1 and 3 kJ/cm^2 in each case), the changes had not saturated at these doses. For instance, it takes a dose of greater than 40 kJ/cm^2 to saturate the UV absorption increases in the case of Fig. 1(a).

In view of these markedly different results, we decided to compare the writing efficiency for in-fiber

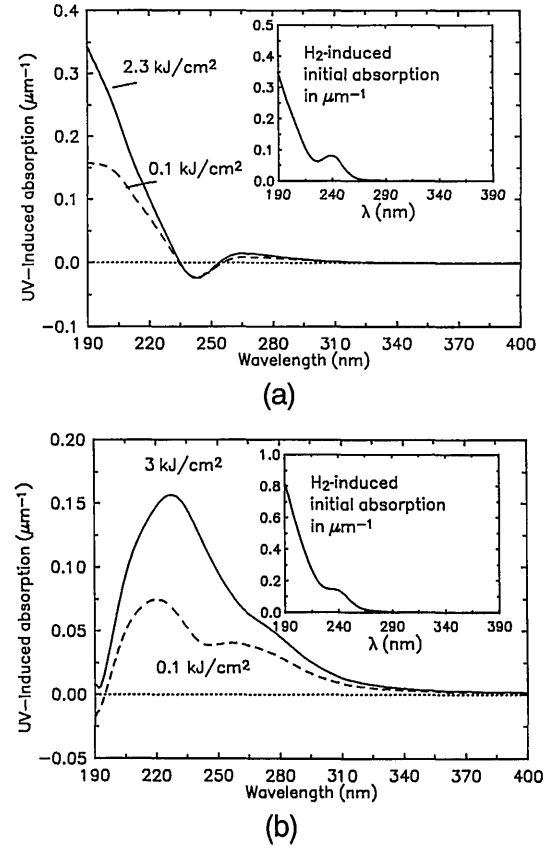

Fig. 2. Spectra of absorption changes induced by UV light in H_2-loaded Ge-doped silica with initial absorption bands (shown in the insets): (a) at 248 nm, (b) at 193 nm. The two curves in each graph correspond to different cumulative UV doses.

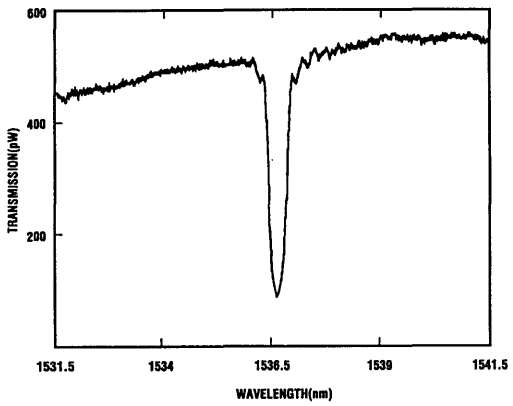

Fig. 3. Spectral transmission of a 3-mm-long, 0.53-μm-period Bragg grating fabricated in Ge-doped optical fiber with 193-nm light from an ArF excimer laser. Repetition rate, 50 pulses/s; 120 mJ/cm^2 per pulse; exposure time, 4 min.

Bragg gratings, using 193- and 248-nm light. The gratings were exposed at 50 pulses/s with doses of 300 mJ/cm^2 per pulse at 248 nm and 120 mJ/cm^2 per pulse at 193 nm. After 4 min of exposure (total UV doses of 1.4 kJ/cm^2), the reflectivity of a 3.0-mm-long grating exposed at 193 nm had reached a maximum of 80%, whereas that of a 3.5-mm-long grating exposed at 248 nm reached only 20% after 6 min (for a total dose of 5.4 kJ/cm^2). In contrast to the 193-nm, the reflectivity of gratings written at 248 nm continues to increase slowly for at least 60 min of irradiation. We show in Fig. 3 the high-quality spectral transmission response of the 80% reflectivity grating written with 193-nm light (a 99.5% reflectivity was achieved with a 6-mm-long device). Therefore, in spite of the fact that the fiber used is likely to have had a bleachable absorption band near 242 nm, the writing efficiency of refractive-index gratings is higher with excitation at 193 nm. With H_2-loaded fiber, the photosensitivity is large at both excitation wavelengths, but preliminary experiments indicate that the same trend is observed, namely, faster saturation with 193-nm radiation.

Both sets of results presented here challenge the standard model of the essential role of the bleaching of a 242-nm band in fiber photosensitivity. In this model, bleaching at 242 nm is accompanied by absorption increases in neighboring bands [as shown in Fig. 2(a)], the net result being a refractive-index increase at longer wavelengths through the Kramers–Kronig relationship.[5,8] Instead, we observe that large absorption changes occur at several wavelengths in the UV and the vacuum UV under strong illumination at both 193 and 248 nm. The presence of an initial absorption based near 242 nm seems to increase the efficiency of 248-nm radiation in producing such changes. On the other hand, we observed that the writing of Bragg gratings in a standard optical fiber is more efficient at 193 nm than at 248 nm.

The physical mechanisms responsible for these findings are not understood at this time. However, the photoinduced absorption changes observed under 193-nm illumination show a strong similarity (but amplitudes larger by several orders of magnitude) to those observed in pure silica, where 220- and 260-nm absorption bands are induced under similar conditions.[13,14] In the case of silica, two-photon absorption (the band gap of silica is ~9 eV, less than the sum of two 6.4-eV photons or two 5.0-eV photons)[14] or the excitation of the tail of an absorption band located between 7 and 8 eV (Ref. 13) is believed to be responsible for generating the carriers involved in the rearrangement of defects observed through the UV absorption changes. This may also be the case here. Finally, preliminary isochronal annealing experiments (30 min at each temperature) show that there is no difference in the thermal stability of gratings fabricated at the two wavelengths: in both cases, the refractive-index modulation has dropped to 90% of its initial value at 300 °C and to 50% near 600 °C.

In conclusion, we have presented results that shed new light on the UV-induced absorption changes occurring in the photosensitivity of Ge-doped silica optical waveguides. In particular, the importance of in-band bleaching at 242 nm is questioned, and we emphasize the need for further studies of photosensitivity with shorter-wavelength sources and spectroscopic measurements in the vacuum UV. Furthermore, we propose the use of a 193-nm laser source (the ArF excimer laser) for the efficient writing of refractive-index patterns in Ge-doped silica (especially optical fibers). An additional advantage of using shorter-wavelength light is the possibility of higher spatial resolution in diffraction-limited applications, such as point-by-point writing.[15]

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